Antifouling Properties of Two Dimensional Molybdenum Disulfide and Graphene Oxide Nanomaterials

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Environmental Significant Statement

Two-dimensional graphene-based nanomaterials including graphene oxide (GO) and reduced graphene oxide (rGO) have shown antibacterial properties, which could be useful for different environmental applications. Many studies also reported the potential application of GO/rGO for antifouling membrane preparation. While graphene-based materials have been extensively studied, recently molybdenum disulfide (MoS$_2$) nanosheets have gained lot of attentions. Most of the research that has focused on MoS$_2$ for application in electronics, catalysis, biomedical and energy related fields. However, its use as an antifouling material has not been extensively explored. MoS$_2$ has extremely low friction as well as low surface roughness and so MoS$_2$ has great potential for antifouling surface preparation. Overall MoS$_2$ showed superior antifouling properties compared to GO in this study. Results indicate that MoS$_2$ may be more suitable for antifouling surfaces in environmental applications. Integration of MoS$_2$ for the preparation of antifouling surface could be applied in different industries such as water filters, ship hulls, biomedical devices, coatings, and paintings.
Antifouling Properties of Two Dimensional Molybdenum Disulfide
and Graphene Oxide

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Abstract

Fouling remains one of the biggest challenges in a myriad of industries such as water filters, ship hulls, biomedical devices, coatings, and paintings. Fouling severely hampers the performance and increase the operation and maintenance costs in industries. There is a critical need to develop antifouling surfaces and two-dimensional (2D) materials, such as graphene oxide (GO) and molybdenum disulfide (MoS$_2$), have shown potential for antifouling surface preparation due to some unique properties. Here, the antifouling properties of these two materials were investigated by observing the deposition kinetics of bacteria and natural organic matter (NOM) using a quartz crystal microbalance with dissipation monitoring (QCM-D). Suwannee River humic acid (SRHA) and *E. coli* K-12 were used as model NOM and bacteria, respectively. Overall MoS$_2$ showed slightly better antifouling properties compared to GO. In most cases, the deposition of NOM and *E. coli* was significantly lower on MoS$_2$ than GO due to the presence of functional groups on GO that bind more easily with the foulants. Deposition of NOM was at least 1.5 times lower on MoS$_2$ surface than GO surface in the presence of both monovalent (Na$^+$) and divalent (Mg$^{2+}$) cations. However, the presence of 0.5 mM divalent cations (Ca$^{2+}$, Mg$^{2+}$) with NOM reduced the antifouling properties of both MoS$_2$ and GO by a factor of $\geq 1.5$ due to a salt bridging effect and reduced energy barrier.
1. Introduction

Two-dimensional graphene-based nanomaterials including graphene oxide (GO) and reduced graphene oxide (rGO) have shown great potential in different environmental applications such as photocatalytic oxidation, contaminant removal, membrane-based separation etc. \(^1\)-\(^3\) Several studies have demonstrated the strong antimicrobial properties of GO against a wide variety of microorganisms, including gram-positive and gram-negative bacterial pathogens, phytopathogens, and biofilm-forming microorganisms.\(^4\), \(^5\) Additionally, GO is hydrophilic, which could result in higher water permeation, making the membrane less susceptible to fouling during filtration.\(^6\), \(^7\) While graphene-based materials have been extensively studied, recently molybdenum disulfide (MoS\(_2\)) nanosheets have gained lot of attentions. MoS\(_2\), a member of the emerging 2D nanomaterial class of transition metal dichalcogenides, has unique electrical, physicochemical and mechanical properties.\(^8\), \(^9\) Despite the significant research that has focused on MoS\(_2\) for application in electronics, catalysis, biomedical and energy related fields, its use as an antifouling material has not been extensively explored. MoS\(_2\) has extremely low friction and low surface roughness.\(^10\), \(^11\) Foulants are less likely to adhere to the MoS\(_2\) surfaces due to this property.\(^12\), \(^13\) The advancement of membrane technology for water filtration is severely hampered by the long-standing problem of fouling, which is caused by the accumulation of foreign substances on the membrane surfaces or inside the membrane pores.\(^14\), \(^15\) Fouling has been found to deteriorate membrane performance causing low water permeability, poor product water quality, high energy consumption, and short membrane life.\(^16\), \(^17\) Biofouling, colloidal fouling, organic fouling and scaling remain the most significant problems for efficient application of nano-filtration and reverse osmosis.\(^18\), \(^19\) Beside fouling in water filtration membrane, fouling also causes serious problem in marine ship hulls due to the presence of more
than 4000 species of marine organisms.\textsuperscript{20-22} Fouling by different proteins and bacteria has also
been reported in biomedical applications, including biosensors, bioanalytical devices, and
implants.\textsuperscript{23, 24}

Before integrating MoS\textsubscript{2} for the preparation of antifouling surface into water filtration
membranes or biomedical devices, it is important to understand the antifouling mechanisms of
this nanomaterial. In this work, the antifouling performance of MoS\textsubscript{2} and GO has been compared
in terms of maximum foulants deposition and foulants deposition rates on those material
surfaces. A quartz crystal microbalance with dissipation monitoring (QCM-D) was used to study
the interactions of MoS\textsubscript{2} and GO with natural organic matter (NOM) and \textit{E. coli} (K-12). NOM is
mainly composed of humic substances and polysaccharides and is common in the aquatic
environment.\textsuperscript{25} \textit{E. coli} K12 is also common in natural water and one of the most commonly used
bacteria strains for fouling studies.\textsuperscript{26, 27} Interaction of these foulants with MoS\textsubscript{2} and GO will thus
give a clear indication of the antifouling properties of the materials. The impact of ion presence
and valence on the attachment of foulants with MoS\textsubscript{2} and GO is also investigated.

2. Materials and Methods

2.1 Preparation of materials

2D GO and MoS\textsubscript{2} were both synthesized using top-down approaches. A modified Hummers’
method was used to synthesize graphene oxide.\textsuperscript{28, 29} Detailed synthesis process of GO is provided
in the supporting information. The MoS\textsubscript{2} nanomaterial used in this study was synthesized using a
lithiation process described elsewhere.\textsuperscript{30} Briefly, Lithium intercalation was achieved by
combining bulk MoS\textsubscript{2} powder and butyllithium in a low vapor and oxygen condition for 2 days
with continuous stirring. The lithiated MoS\textsubscript{2} was rinsed extensively with hexane, filtered, and
exfoliated by the addition of deionized water and bath sonication. The resulting dispersion was
centrifuged to remove any unexfoliated material. The supernatant was further dialyzed for 7 days
in a bath of deionized water to remove residual lithium and hexane.

2.2 Characterization of materials

AFM imaging was used to determine the surface roughness of the materials. X-ray photoelectron
spectroscopy (XPS) was done to determine the amount of functional groups present in GO and
MoS$_2$ materials. Hydrodynamic diameter ($D_h$) and zeta potential ($\zeta$-potential) of the materials
and the E. coli were also measured for the calculation of DLVO theory (supporting information).
Contact angle measurement also done to determine the hydraphilicity of GO and MoS$_2$.

2.2.1 AFM and XPS analysis

The surface roughness of GO, MoS$_2$ and PLL were measured by atomic force microscopy
(AFM) using a similar procedure on previously published work.\textsuperscript{28, 29} Si wafers with a 100 nm
thick oxide surface were used as substrates. At first, Si wafers were washed by acetone and
isopropanol, and then rinsed with deionized (DI) water. For preparing a self-assembled
functionalized monolayer, the Si wafers were put in a 2.5 mM (3- amino propyl) triethoxysilane
(APTES) solution for 30 minutes and then rinsed with DI water again. Then immediately after
drying with N$_2$, a 5 mg/L GO/MoS$_2$/PLL drop was placed on the surface. After waiting for 10
min, the sample was rinsed with DI water and dried with N$_2$. The sample was further heat treated
at 250°C for 30 min for removing the residual APTES. AFM images were taken using a Thermo
Microscopes Auto probe CP-Research AFM in tapping mode with conical, symmetric probes
(Budget Sensors, All-In-One, cantilever B). Images were taken at several random locations on
each sample and showed little variation.
Samples for XPS analysis were prepared using a procedure similar to previously published work. XPS samples (approximately 5 mg) were prepared by vacuum filtration of the material dispersions onto a PTFE membrane filter with a 0.1 µm pore size (Millipore). The film was allowed to settle for 15 minutes, rinsed with 30 mL DI water, and allowed to dry in air. XPS spectra were collected using a Thermo Scientific ESCALAB 250Xi. XPS spectra were then corrected for background and fitted for peaks manually.

### 2.2.2 Electrokinetic and Hydrodynamic Characterization

Hydrodynamic diameter ($D_h$) and zeta potential ($\zeta$-potential) were measured using a Zeta Sizer Nano ZS (Malvern Instruments, Worcestershire, U.K.), following well-established techniques. ZetaSizer Nano ZS was equipped with a monochromatic coherent He-Ne laser with a fixed wavelength of 633 nm. ZetaSizer Nano ZS uses the Stokes–Einstein equation to calculate the intensity averaged (average size) hydrodynamic diameter ($D_h$). Zeta potentials ($\zeta$-potential) of the GO, MoS$_2$ and $E. coli$ were also measured using a ZetaSizer Nano ZS instrument, which employs phase analysis light scattering (PALS) to measure the electrophoretic mobility of charged particles. ZetaSizer Nano ZS uses the Smoluchowski equation to calculate $\zeta$-potential from electrophoretic mobility (EPM).

### 2.2.3 Contact angle measurement

25 µL of GO and MoS$_2$ dispersions at a concentration of 0.02 mg mL$^{-1}$ was drop cast onto a clean SiO$_2$ wafer. A 5 µL water droplet was placed onto the surface and the contact angle was measured within 30 seconds using a Krüss DSA100 Drop Size Analyzer. Error bars represent one standard deviation ($n = 3$).
2.3 Aquatic chemistry

Suwannee River humic acid (Standard II, International Humic Substances Society) was used to prepare the natural organic matter (NOM) suspension at a concentration of 10 mg/L. *Escherichia coli* (*E. coli*, MG1655, K-12) was supplied by the *E. coli* Genetic Resource Center of Yale University. GO or MoS$_2$ surfaces on gold crystals for QCM-D measurements were prepared by modifying the gold sensors with cationic Poly-L-lysine hydrobromide (PLL, molecular weight 70 000–150 000 Da by viscosity, P-1274, Sigma Aldrich, St. Louis, MO). PLL was dissolved in HEPES buffer (pH 7.4) made from 10 mM N-(2-hydroxyethyl) piperazine-N-2-ethanesulfonic acid (Sigma), 100 mM NaCl and deionized water and was stored at 4 °C. The final concentration of the stock PLL solution was 0.1 g L$^{-1}$. The gold substrate cells were exposed to the PLL stock solution for 15-20 min to create a homogeneous layer. Calcium chloride (CaCl$_2$.2H$_2$O, CAS: 10035048), sodium chloride (NaCl, CAS 7647-14-5) and magnesium chloride (MgCl$_2$.6H$_2$O, CAS: 7791-18-6) were used to prepare salt solutions. 10 mM NaCl and 0.5 mM CaCl$_2$/MgCl$_2$ were used for the experiments. 10 mg/L GO and 50 mg/L MoS$_2$ were prepared from the stock sample solutions.

2.4 Bacterial Strains and Growth Studies

*Escherichia coli* MG1655 used in this study was pre-cultured, cultured and then harvested following the standard procedure.$^{35}$ First, a sterile tip was used to pick up bacteria from the petri dish, after which the tip with bacteria was stirred in 5 mL of lysogeny broth (LB-Miller). Then it was incubated overnight at 37 °C. To culture, 2 mL of pre-culture was added to 200 mL of fresh LB broth and incubated for 24 hr at 37 °C to reach the stationary phase of the bacterial cells. For
harvesting, 40 mL of culture liquid was poured into a centrifuge tube and then centrifuged at
3689 g for 15 min at 4 °C. The supernatant was discarded and the pellet was resuspended by
adding 10 mL of 10 mM NaCl and vortexing. Then it was again centrifuged at 3689 g for 15 min
at 4 °C and the same procedure was followed to resuspend the pellet in 10 mM NaCl. The cell
collection used in this study was ~10^6 cells per mL. The final cell suspensions were made in
the background solution (10 mM Na^+ or 0.5mM Ca^{2+}).

2.5 Fouling study

2.5.1 Fouulant deposition with nanomaterial coated surface

Gold sensors were coated with the nanomaterial of interest using the same procedure from
previous studies (Fig. S1). Briefly, to achieve a stable baseline reading, the gold sensor
surface was rinsed with milli-Q (MQ) water until the changes in frequency and dissipation were
<0.3 Hz and <0.2*10^{-6} respectively for 10 min. (Stage I). The QCM-D system was equilibrated
with HEPES buffer in 100 mM NaCl solution for 30 min at a flow rate of 0.1 mL/min (Stage II).
PLL in HEPES buffer solution was introduced at 0.1 mL/min (Stage III). The PLL layer was
rinsed with HEPES for 20 min to remove the unadsorbed PLL (Stage IV). Finally, 1 mM NaCl
solution (background electrolyte) was used to remove the buffer at a flow rate of 0.1 mL/min for
30 min (Stage V). 10 mg/L GO or 50 mg/L MoS_2 was deposited on the PLL coated surface by
flowing at a rate of 0.1 mL/min for at least 30 min (Stage VI). Similar type of approach was
used to deposit nanomaterials on QCM-D sensors in previous studies. MoS_2 showed slow
deposition on PLL and thus a higher concentration of MoS_2 was employed to achieve a fully
coated sensor in a reasonable time period. The sensors were exposed to the GO and MoS_2
solutions until maximum frequency was achieved and the frequency shift became stable
indicating full coverage of both materials on the PLL surface. All the fouling experiments were
done on bare PLL surface also to compare the results with the GO/MoS$_2$ coated surface (Fig. S2). This was done to confirm that no PLL was exposed during the fouling study and the foulants only interacted with GO and MoS$_2$ surfaces. Any exposed PLL even after GO/MoS$_2$ coating would result into higher frequency shifts and dissipation changes like bare PLL surface experiment. To test the antifouling properties, NOM and *E. coli* were injected across the nanomaterial-coated surface at a flow rate of 0.1 mL/min until the QCM-D showed a stable frequency shift. QCM-D cells and sensors were cleaned following the Q-sense cleaning protocols before and after the experiment. Briefly, 5 mL of Hellmanex III (Fisherbrand™, cleaning concentrate) was flowed through the tubes to the QCM-D cells followed by 20 mL of Milli-Q water to clean the cells. The gold sensors were soaked in a solution of 5:1:1 Milli-Q water, NH$_4$OH and H$_2$O$_2$ at 75 ± 5 °C for 5 min. The sensors were air dried and placed in a UV chamber for 20 min. All the fouling study were replicated three times and results are summarized in table S1.

### 2.5.2 Deposition and release study using QCM-D

The deposition kinetics of NOM and *E. coli* were determined from the frequency shifts monitored by QCM-D from which the deposition rate and attachment efficiency can be calculated.$^{38}$ Shifts in frequency and dissipation were monitored at the third overtone. Initial deposition rates $r_f$ and $r_D$ are defined as rates of frequency and dissipation shift in a time period respectively (Eq. 1 and 2)$^{36, 39}$:

\[
\begin{align*}
  r_f &= \left( \frac{d\Delta f(3)}{dt} \right)_{t \to 0} \\
  r_D &= \left( \frac{d\Delta D(3)}{dt} \right)_{t \to 0}
\end{align*}
\]
Attachment efficiency gives information on how fast the foulants deposit on the material surface with respect to bare polymer surfaces (PLL).\textsuperscript{36, 39} It is a good indicator for comparing the antifouling performance of GO and MoS\textsubscript{2}. The deposition attachment efficiency ($\alpha_D$) is calculated from deposition rates:

$$
\alpha_D = \frac{r_f}{(r_t)_{PLL}} = \left| \frac{\left( \frac{d\Delta f_{(3)}}{dt} \right)_{PLL}}{\left( \frac{d\Delta f_{(3)}}{dt} \right)_{t\to0}} \right|,
$$

(3)

NOM and \textit{E. coli} were directly deposited on PLL surfaces as a control to investigate the deposition behavior of foulants. In Eq. 3, the denominator represents the rate of frequency shift obtained with bare polymer surface conditions. An attachment efficiency of $<1$ indicates the slower foulant deposition rate on the surfaces functionalized with GO or MoS\textsubscript{2} when compared to a bare polymer surface, which is expected as PLL is positively charged and most likely to interact more with negatively charged foulants. Attachment efficiencies of foulants on GO and MoS\textsubscript{2} were calculated using Eq. 3 and then the antifouling performance of GO and MoS\textsubscript{2} was directly compared.

### 3. Results and discussion

#### 3.1 Characterization of GO and MoS\textsubscript{2}

The average hydrodynamic diameters (Table 1) of GO and MoS\textsubscript{2} in deionized water were $385.3 \pm 7.58$ nm and $153.5 \pm 1.67$ nm, respectively. Zeta potentials (Table 1) of GO and MoS\textsubscript{2} in deionized water were $-41.33 \pm 0.5$ mV and $-40.34 \pm 0.76$ mV, respectively. The highly negative zeta potentials of MoS\textsubscript{2} and GO indicate that they are moderately stable in water. Additionally, this suggests that MoS\textsubscript{2} and GO functionalized surfaces could effectively repel foulants due to
the negative surface charge of most foulants. Representative atomic force microscopy (AFM) images of GO and MoS$_2$ are shown in figure 1. The surface roughness of the GO and MoS$_2$ on PLL coated gold sensors were 2.5 ± 0.3 nm and 2.4 ± 0.3 nm, respectively. The surface roughness of a bare PLL surface was found to be 5.1 ± 1.2 nm. From these measurements it is clear that the deposition of the 2D materials reduced the roughness of the polymer surface. XPS spectra (Fig. 2) of GO C1s showed three convoluted peaks corresponding to C-C (~284.8 eV), C-O (~286.8 eV) and O-C=O (288.5 eV). For MoS$_2$ three characteristic peaks were seen in the Mo3d scan corresponding to the Mo3d 3/2 (~232.5 eV), Mo3d 5/2 (~229 eV) and S2s (~226.5 eV) and the characteristic doublet peak in the S2p spectrum. These XPS data confirm that there was no oxygen containing functional groups in MoS$_2$ structure. Contact angle measurement results (Fig. S3) confirms both GO and MoS$_2$ used in this study were hydrophilic. GO had an contact angle of 25± 5.4 while the contact angle of MoS$_2$ was 42±4.6 suggesting GO was slightly more hydrophilic than the MoS$_2$.

3.2 Deposition kinetics of natural organic matter (NOM) on GO and MoS$_2$ surfaces

The maximum frequency shift on QCM-D was used to determine the maximum deposition of NOM on both surfaces under experimental conditions. The maximum deposition, thus, is an indication of the fouling caused by NOM on GO and MoS$_2$ surfaces. Following injection of NOM onto the nanomaterial functionalized surfaces, a slight frequency shift was observed on the GO surface (<1.5 Hz), and even less frequency shift was observed on the MoS$_2$ surface, indicating that MoS$_2$ will be less prone to fouling from NOM (Fig. 3A, S3, S4). In fact, the change in frequency shift during NOM deposition on MoS$_2$ is negligible (Fig. S4) as small frequency shift (~0.5 Hz) could be observed due to vibration on the gold sensor. Due to the high zeta potential of GO and MoS$_2$ and negative charge of NOM, the interaction of NOM with the
material surfaces will be minimal due to electrostatic repulsion, and thus there is hardly any deposition of NOM on the material surfaces.

NOM attaches to a GO and MoS$_2$ functionalized surfaces 70% and 80% more slowly on average than a bare polymer surface (favorable condition) respectively (Fig. 3B), suggesting NOM deposits on both the surfaces at a similar rate. However, less NOM attachment makes MoS$_2$ preferable to GO as an antifouling surface. These results agree with previous studies which have shown that interactions between GO surfaces and NOM are electrostatically unfavorable$^{39}$ as NOM is negatively charged under environmentally relevant conditions.$^{40}$ No significant deposition of NOM was observed on the MoS$_2$ surface despite a zeta potential similar to GO. The difference in their interactions with NOM is most likely due to the presence of functional groups on GO that can interact with NOM. Previously it has been shown that GO deposits more readily on surfaces that have been coated with NOM due to the high amount of hydroxyl and carboxyl functional groups on GO that readily bind with functional groups of NOM.$^{39}$ Lack of functional groups on MoS$_2$ may be responsible for lower interactions with NOM.

3.3 Interactions of GO and MoS$_2$ with natural organic matter (NOM) in the presence of monovalent ions

The maximum shift observed was 1.65 Hz on the GO surface and 1.52 Hz on the MoS$_2$ surface (Fig. 4A, S6, S7). Though the frequency shifts were not significantly different, the initial deposition rate of NOM in the presence of Na$^+$ was 0.98 Hz/min (Fig. S6) on a GO surface and 0.64 Hz/min (Fig. S7) on an MoS$_2$ surface. Using this deposition rate, the attachment efficiencies (Fig. 4B) of NOM were found to be 57% and 36% on GO and MoS$_2$ surfaces, respectively, indicating that NOM deposits on MoS$_2$ more slowly than on GO. The slower deposition rate of NOM on MoS$_2$ makes it a more advantageous material choice than GO for antifouling
properties. The increase in the overall deposition of NOM in this case is mainly due to reduced electrostatic repulsion and the effect of charge neutralization caused by the presence of Na\(^+\) ions. In particular, in the presence of Na\(^+\), the energy barrier between NOM and the material surfaces is reduced, allowing the functional groups of NOM to attach to the material surfaces. In the presence of NaCl, increased interactions between carbon-based nanomaterials with NOM were found in other studies.\(^{37, 41}\) The increased frequency shift and higher attachment efficiency of NOM in Na\(^+\) to the GO and MoS\(_2\) surfaces clearly indicate that Na\(^+\) certainly plays a role in the deposition of NOM.

### 3.4 Interactions of GO and MoS\(_2\) with natural organic matter (NOM) in the presence of divalent cations

From the values of maximum frequency shift, it is clear that the deposition of NOM on both material surfaces in the presence of divalent cations is higher than in the presence of monovalent ions (Fig. S8, S9). The average maximum shifts observed for NOM in Ca\(^{2+}\) were 5.97 Hz (Fig. S8) and 5.37 Hz (Fig. S9) on GO and MoS\(_2\), respectively, and in Mg\(^{2+}\) the maximum frequency shifts were 4.60 Hz and 3.81 Hz on GO and MoS\(_2\), respectively, (Fig. 5A). The average attachment efficiencies (Fig. 5B) of NOM in the presence of Ca\(^{2+}\) were 66\% and 41\% on GO and MoS\(_2\) surfaces, respectively. The attachment efficiencies of NOM in Mg\(^{2+}\) were 73\% and 39\% on GO and MoS\(_2\) surfaces, respectively indicating the superior antifouling properties of MoS\(_2\) over GO (Fig. 5B). The difference in antifouling performance between GO and MoS\(_2\) was more significant in case of NOM in Mg\(^{2+}\). On the other hand, Ca\(^{2+}\) in NOM caused the fouling on both GO and MoS\(_2\) surfaces at a similar rate. Moreover, increased values of both maximum frequency shifts and attachment efficiencies suggest that electrostatic repulsion between the NOM and the GO or MoS\(_2\) surface is reduced in the presence of Ca\(^{2+}\) or Mg\(^{2+}\). This decrease in
the energy barrier between NOM and the surface allows the NOM to come into close contact
with the material surfaces in the presence of divalent cations. This higher deposition of NOM can
also be attributed to salt bridging caused by the divalent cations. This bridging effect is well
documented in the literature.\textsuperscript{42, 43} Chen and Elimelech observed a slightly higher interaction of
fullerenes and Suwanee River humic acid (SRHA) on bare silica in the presence of CaCl\textsubscript{2} due to
SRHA macromolecules undergoing complex formation with Ca\textsuperscript{2+} that reduces electrostatic and
steric effects.\textsuperscript{37} Chowdhury et al. found a similar bridging effect of divalent cations during the
interaction of GO and Suwanee River fulvic acid (SRFA) using QCM-D.\textsuperscript{39} It is clear from this
study that the antifouling ability of both GO and MoS\textsubscript{2} decreases significantly when NOM is
present with divalent cations in solution. The bridging effect and decrease in the energy barrier
help NOM to deposit onto the material surfaces in the presence of divalent cations. Overall,
average deposition of NOM and attachment efficiency were slightly lower on MoS\textsubscript{2} than GO
especially in the case of NOM in Mg\textsuperscript{2+}.

3.5 Interactions of GO and MoS\textsubscript{2} with \textit{E. coli}

The maximum frequency shift during \textit{E. coli} deposition in the presence of 10 mM NaCl is shown
in figures 6A, S10 \& S11. After 30 min of \textit{E. coli} injection, \textit{E. coli} in Na\textsuperscript{+} showed an average
frequency shift of 7.39 Hz (Fig. S10) on GO surfaces while the average shift was 5.59 Hz (Fig.
S11) on MoS\textsubscript{2} surfaces, indicating that overall deposition of \textit{E. coli} was slightly lower on MoS\textsubscript{2}
than GO in this case also. Figure 6B shows that the average attachment efficiencies of \textit{E. coli} in
Na\textsuperscript{+} were 71\% and 62\% on GO and MoS\textsubscript{2} surfaces, respectively. However, it has been found the
interaction of \textit{E. coli} with GO and MoS\textsubscript{2} surfaces was not significantly different unlike the
interaction of NOM. Nevertheless, low attachment efficiency for GO and MoS\textsubscript{2} indicates an
improvement of the antifouling properties of both the surface. Poitras and Tufenkji reported that
QCM-D underestimates the mass adsorbed on the crystal surface for “soft mass” such as bacterial cells.\textsuperscript{44} They reported that along with frequency shift, the dissipation shift also changed significantly during \textit{E. coli} deposition. Though the interaction of \textit{E. coli} is highly surface dependent, in this study, significant dissipation shit was also noticed. The changes in dissipation shift on GO and MoS\textsubscript{2} surfaces were $15.52\times 10^{-6}$ (Fig. S10) and $12.13\times 10^{-6}$ (Fig. S11) on average respectively. It is important to report that the increase in dissipation shift during the \textit{E. coli} deposition was much higher than the NOM deposition which indicates that the \textit{E. coli} creates a softer layer than NOM on 2D material surfaces.

\textit{E. coli}, which are gram negative bacteria, have an outer covering of lipopolysaccharides that impart a strongly negative charge to the surface of the gram negative bacterial cells.\textsuperscript{45} We hypothesize that any attachment of \textit{E. coli} to the material surfaces that did occur might be due to extracellular polymeric substances (EPSs).\textsuperscript{46, 47} Previously it has been observed that stationary phase cells cultivated in LB media have less negative charge than the exponential phase cells and tend to aggregate more,\textsuperscript{48} which may also contribute to the cell attachment on the material surfaces. In another study, it has been reported that \textit{E. coli} MG1655 aggregates more in the stationary phase due to high protein content on free EPS.\textsuperscript{49} Overall, MoS\textsubscript{2} performed as good as GO in terms of average deposition and attachment efficiency against \textit{E. coli}.

4. Mechanisms involved in the interaction of foulants on GO and MoS\textsubscript{2} surfaces

4.1 Influence of surface charge and salt bridging

Figures 7 and S13 represent the overall mechanisms in interactions of MoS\textsubscript{2} and GO with NOM and bacteria, respectively. Interaction energy between \textit{E. coli} and GO and MoS\textsubscript{2} in the presence of monovalent ions was calculated using DLVO theory (Supporting Information). The zeta
potential and hydrodynamic size of *E. coli* in 10mM NaCl were -44.2 mV and 2 µm, respectively, under experimental conditions. Result from DLVO theory (Figure S12) suggest that the energy barrier between the *E. coli* and the 2D material surfaces was very high (2000 KT). The high negative surface charge of the 2D materials creates unfavorable conditions for NOM deposition also. However, there was still deposition of the foulants on the material surfaces particularly on GO due to salt bridging. The presence of divalent cations (Ca$^{2+}$, Mg$^{2+}$) contributes to the NOM-NOM interaction$^{50, 51}$ and may also causes deposition of foulants as Ca$^{2+}$ or Mg$^{2+}$ could work as a linker between NOM and GO or MoS$_2$. Furthermore, divalent cations can reduce electrostatic and steric effects and influence the interaction of foulants on the material surfaces.$^{37, 39, 42}$ Due to the large amount of functional groups, GO is more prone to salt bridging. On the other hand, lack of functional groups on MoS$_2$ makes the surface unfavorable for salt bridging, which results in slightly lower attachment of foulants on MoS$_2$ than GO. Furthermore, the energy barriers between foulants and material surfaces fall at a separation distance of 20-22 nm (secondary minimum) and the interaction energy is not repulsive after that point (Fig S12). In the case of *E. coli*, the secondary minimum starts at 23 nm with the maximum attraction energy of 1.32 KT at 29 nm (Fig. S12). This indicates that the higher energy barrier is not effective beyond that range and other interactions, such as the presence of functional groups and surface roughness, may play the dominant role.

Most of the foulants in nature are negatively charged and thus negatively charged membranes can create electrostatic repulsion between foulants co ions and membranes surface.$^{52}$ However, the electrostatic repulsion could be overcome by the foulants due to secondary minimum where hydrogen bond, van der Waals force dominate. Few recent studies have reported that sometimes charge neutral surfaces perform better as antifouling surfaces.$^{53, 54}$
4.2 Influence of functional groups and surface roughness

NOM contains carboxyl, hydroxyl, and amino functional groups\textsuperscript{55-57} and GO contains primarily epoxy, hydroxyl, and carboxyl functional groups (Fig. 2 and S13).\textsuperscript{58, 59} NOM molecules have been reported to adsorb on GO via hydrogen bonds, Lewis acid–base, and π-π interactions (Fig. S13).\textsuperscript{56} Hydroxyl functional groups of NOM can form hydrogen bonds with oxygen-containing functional groups of GO.\textsuperscript{56, 60} On the other hand, lack of functional groups (Fig. 2) on MoS\textsubscript{2} will reduce the interactions of NOM, which was confirmed by the lower attachment of NOM with MoS\textsubscript{2} than GO. However, hydrophobic interactions between the foulants and the MoS\textsubscript{2} may be responsible for foulant deposition on MoS\textsubscript{2} surfaces (Fig. 7).\textsuperscript{61} NOM has both hydrophilic and hydrophobic fractions and the hydrophobic humic substances constitute the major NOM fraction.\textsuperscript{62} MoS\textsubscript{2} is hydrophobic in nature and can interact with the hydrophobic parts of the foulants. \textit{E. coli} mainly attach to the material surfaces due to the extracellular polymeric substances (EPSs) from their outer surface. EPSs consisting of polysaccharides, proteins and other biopolymers also have functional groups like carboxyl, hydroxyl, amino functional groups on their structures (Fig. 7 & S13). Presence of these functional group help \textit{E. coli} to bind with GO and MoS\textsubscript{2} functionalized surfaces (Fig. 7 & S13). Presence of functional groups in GO forms hydrogen bond with the lipopolysaccharides (LPS) of Gram-negative (\textit{E. coli}) bacteria.\textsuperscript{63, 64} Also, physisorbed bulk water on MoS\textsubscript{2} surfaces may form hydrogen bond with the –OH functional groups of polysaccharides.\textsuperscript{64} Constituents of EPSs have different patches or domains that can be hydrophobic, hydrophilic, positively or negatively charged nature.\textsuperscript{65, 66} Complex structure of those proteins and polysaccharides favor the \textit{E. coli} deposition on both material surfaces. However, deposition of \textit{E. coli} on MoS\textsubscript{2} surface was significantly lower due to lack of functional groups.
In most cases, the foulants showed slightly less attachment to MoS\textsubscript{2} surfaces than to GO surfaces. However, additional mechanisms may also play a role in this difference in antifouling behavior. In particular, surface roughness is an important parameter to consider in any fouling study. The surface roughness of the PLL, GO on PLL and MoS\textsubscript{2} on PLL surfaces used in this study were measured to be 5.1 ± 1.2 nm, 2.5 ± 0.3 nm and 2.4 ± 0.3 nm, respectively. This indicates that the addition of GO and MoS\textsubscript{2} creates a smoother surface than the bare polymer surface. This higher roughness value may contribute to the higher fouling occurring on the bare polymer surface in addition to the contribution of the positive charges on polymer surface. Rough surfaces are more susceptible to fouling as foulants deposit in valleys, making it difficult to remove the foulants by hydrodynamic force. \cite{67, 68} Both the GO and MoS\textsubscript{2} surfaces showed negligible differences in roughness, and thus the functional groups of GO are likely responsible for lower antifouling properties compared to MoS\textsubscript{2}.

5. Conclusions

GO has been a research interest for preparing antifouling membranes and surface for long time. Overall, from this study, it was found that MoS\textsubscript{2} performs significantly better than GO under most of the fouling conditions investigated in this study. MoS\textsubscript{2} shows more potential for antifouling applications than GO due to lower interactions with foulants on MoS\textsubscript{2}. Better antifouling property of MoS\textsubscript{2} could certainly take over GO for preparation of antifouling surfaces in near future. Ca\textsuperscript{2+} and Mg\textsuperscript{2+} can play a significant role in bridging with foulant molecules and GO and MoS\textsubscript{2} functionalized surfaces. Higher frequency shifts observed in QCM-D suggest that the presence of Ca\textsuperscript{2+} and Mg\textsuperscript{2+} in natural water results in higher deposition of foulants that may impede high water flux and thus the efficiency of the membrane during water filtration. Monovalent ions have less effect on the accumulation of foulants on the material surfaces.
Additionally, *E. coli* showed deposition on both GO and MoS$_2$ surfaces. *E. coli* also creates a softer layer on the material surfaces than NOM confirmed by the higher dissipation shift change on QCM-D during *E. coli* deposition on GO and MoS$_2$ surfaces. Results indicate that MoS$_2$ may be more suitable for antifouling surfaces and membrane applications.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgments**

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**Supporting Information Available**

Additional figures and tables are available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).
Table 1. Average size, zeta potential, mobility and polydispersity index of the GO and MoS\textsubscript{2} dispersions.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Average Zeta Potential (mV)</th>
<th>Average Mobility (µmcm/Vs)</th>
<th>Average Size (d.nm)</th>
<th>PdI</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO in MQ water</td>
<td>-41.33±0.5</td>
<td>-3.24±0.04</td>
<td>385.3±7.58</td>
<td>0.49±0.05</td>
</tr>
<tr>
<td>MoS\textsubscript{2} in MQ water</td>
<td>-40.34±0.76</td>
<td>-3.16±0.06</td>
<td>153.5±1.67</td>
<td>0.22±0.01</td>
</tr>
</tbody>
</table>
Figure 1. AFM images of GO and MoS$_2$ on SiO$_2$. The flakes are mainly monolayer or bilayer with a wide range of lateral sizes.
Figure 2: XPS spectra of GO and MoS$_2$. Three convoluted peaks corresponding to C-C (~284.8 eV), C-O (~286.8 eV) and O-C=O (288.5 eV) in GO C1s spectra confirms presence of oxygen containing functional groups on GO structure. XPS spectra of MoS$_2$ did not show any indication of oxidation. The characteristic 3 peaks in the Mo3d scan corresponding to the Mo3d 3/2 (~232.5 eV), Mo3d 5/2 (~229 eV) and S2s (~226.5 eV) and the characteristic doublet peak in the S2p spectrum were found on XPS of MoS$_2$. 
Figure 3. (A) Maximum frequency shift of GO and MoS$_2$ surfaces against NOM without any salts on QCM-D. MoS$_2$ showed the least NOM attachment on its surface. Error bars represent the standard deviation of the experimental results (98% confidence interval). (B) Attachment efficiency of NOM on both of the surfaces (93% confidence interval).
Figure 4. (A) Maximum frequency shift of GO and MoS$_2$ surfaces against NOM in presence of 10 mM NaCl on QCM-D. NOM in 10 mM NaCl showing slightly higher frequency shifts on both the material surfaces indicated higher deposition compared to NOM with any salts. Error bars represent the standard deviation of the experimental results conducted on different cells of QCM-D (<90% confidence interval). (B) Attachment efficiency of NOM in 10 mM NaCl on GO and MoS$_2$ (99% confidence interval).
Figure 5. (A) Maximum frequency shift of GO and MoS$_2$ surfaces against NOM with the presence of 0.5 mM divalent cations on QCM-D (93% confidence interval for CaCl$_2$ & 99% confidence interval for MgCl$_2$). (B) Attachment efficiency of NOM in 0.5 mM CaCl$_2$ (<90% confidence interval) and 0.5 mM MgCl$_2$ (100% confidence interval) on both GO and MoS$_2$ surfaces. Higher frequency shift and attachment efficiency indicate higher and faster accumulation of NOM on the material surfaces in the presence of divalent ions.
Figure 6. (A) Maximum frequency shift of *E. coli* in 10 mM NaCl on both GO and MoS$_2$ surfaces (90% confidence interval). (B) Attachment efficiency of *E. coli* in 10 mM NaCl on both GO and MoS$_2$ surfaces (<90% confidence interval).
Figure 7. Mechanisms of interactions of MoS$_2$ with NOM and $E. \text{ coli}$. Absence of functional groups in MoS$_2$ structure makes unfavorable condition for foulants deposition. Van der Waals interactions and hydrophobic interactions have been reported to form between NOM and MoS$_2$. Sticky polymeric substances from $E. \text{ coli}$ show high affinities to the MoS$_2$ surface.


17. K. Listiarini, W. Chun, D. D. Sun and J. O. Leckie, Fouling mechanism and resistance analyses of systems containing sodium alginate, calcium, alum and their combination in


